ARL 68-0057
MARCH 1968

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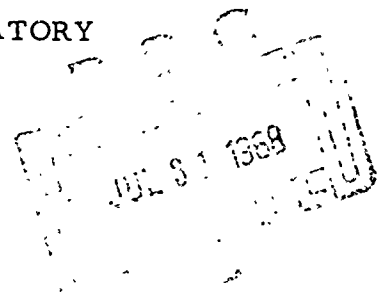
THERMODYNAMICS OF THE TUNGSTEN-OXYGEN SYSTEM

(Reprinted from Trans of the Metallurgical Soc. of AIME, Vol. 239,
pp. 1901-1905, December 1967)

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Project No. 7021

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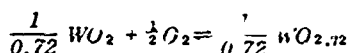
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Thermodynamics of the Tungsten-Oxygen System
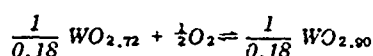
F. E. Rizzo, L. R. Bidwell, and D. F. Frank

The solid electrolyte galvanic cell technique was used to measure the $\Delta G°$ of various reactions of the W O system in the temperature range 700° to 1000°C. The results may be represented by the following linear equations:
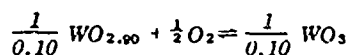
$$\tfrac{1}{2} W + \tfrac{1}{2}O_2 \rightleftharpoons \tfrac{1}{2}WO_2$$
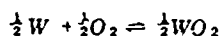
$$\Delta G_I° = -68,660 + 20.31\ T\ (°K) \pm 300\ cal$$

$$\tfrac{1}{0.72} WO_2 + \tfrac{1}{2}O_2 \rightleftharpoons \tfrac{1}{0.72} WO_{2.72}$$

$$\Delta G_{II}° = -59,640 + 15.01\ T\ (°K) \pm 300\ cal$$

$$\tfrac{1}{0.18} WO_{2.72} + \tfrac{1}{2}O_2 \rightleftharpoons \tfrac{1}{0.18} WO_{2.90}$$

$$\Delta G_{III}° = -67,860 + 24.21\ T\ (°K) \pm 300\ cal$$

$$\tfrac{1}{0.10} WO_{2.90} + \tfrac{1}{2}O_2 \rightleftharpoons \tfrac{1}{0.10} WO_3$$

$$\Delta G_{IV}° = -56,765 + 26.76\ T\ (°K) \pm 500\ cal$$

The measured free-energy changes varied slightly with purity. These results differ significantly from earlier electromotive-force measurements. Excellent agreement was obtained with recent gas equilibration measurements. The present results do not support the presence of W_3O.

THE poor high-temperature oxidation resistance of the refractory metals becomes an important problem as higher operating temperatures are sought. A meaningful analysis of their oxidation behavior requires a knowledge of the phases that can appear during oxidation as well as their relative stability.

Although several extensive investigations have been carried out to obtain this information for the W-O system,[1-10] serious inconsistencies still remain. First, the standard free energies of formation ($\Delta G°$) determined in recent studies which used the solid electrolyte galvanic cell technique[6,7,9] differ significantly from those obtained primarily from gas equilibration measurements.[1,3,4,10] The disagreement is especially large for the highest oxides. These data have been used to predict the decomposition temperatures of $WO_{2.72}$ and $WO_{2.90}$.[1] A considerable extrapolation is required, resulting in a large uncertainty in the decomposition temperatures. Second, Bousquet and Perachon[3] have presented convincing evidence, obtained by gas equilibration measurements, in support of the long-contested existence of W_3O. Phillips and Chang,[11] on the other hand, were not able to observe this phase under similar experimental conditions.

The purposes of this work, which is part of a continuing investigation of the W-Mo system, were to resolve the discrepancies between the $\Delta G°$ measured by gas equilibration and solid electrolyte galvanic cell techniques, to extend the latter measurements to lower temperatures, to redetermine the $WO_{2.72}$ and WO_2 decomposition temperatures, and to apply the more sensitive electromotive-force method to the question of the existence of W_3O.

I) EXPERIMENTAL PROCEDURE

The measurement of $\Delta G°$ of reaction by the use of calcia-stabilized zirconia solid electrolyte galvanic cells has been described previously.[12] The method is based on the measurement of the difference in chemical potential of oxygen between an electrode containing the two oxides of interest and a reference electrode of known oxygen activity.

Two different types of cell holders were used in this study. The first type of apparatus has been described earlier.[12] It consisted of two solid electrodes separated by a disc of electrolyte. Both electrodes were exposed to the same stream of purified helium. With this design a gaseous transport of oxygen between the two electrodes is possible. The second type of apparatus, which has also been described earlier,[14] effectively separated the two electrode atmospheres. It utilized a closed-end impervious, calcia-stabilized zirconia tube that was open to the atmosphere. The tube served as an electrolyte for the cell and provided a means for separating the anode compartment, which was held under a static vacuum, from an air reference cathode.

The cells and reactions of interest are described in Table I. High-purity tungsten metal was obtained from the Fansteel Metallurgical Corp. and the Allied Chemical Corp. Table II contains an analysis of each material. WO_3 was prepared by oxidizing the metal in air at approximately 600°C in high-purity recrystallized alumina boats and by the dehydration of reagent-grade tungstic acid in alundum boats. The two methods of preparing WO_3 resulted in slightly different purities.

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Table I

Cell	Virtual Reaction*	
W, WO_2/electrolyte/reference	$\tfrac{1}{2} W + \tfrac{1}{2} O_2 \rightleftharpoons \tfrac{1}{2} WO_2$	I
WO_2, $WO_{2.72}$/electrolyte/reference	$\tfrac{1}{0.72} WO_2 + \tfrac{1}{2} O_2 \rightleftharpoons \tfrac{1}{0.72} WO_{2.72}$	II
$WO_{2.72}$, $WO_{2.90}$/electrolyte/reference	$\tfrac{1}{0.18} WO_{2.72} + \tfrac{1}{2} O_2 \rightleftharpoons \tfrac{1}{0.18} WO_{2.90}$	III
$WO_{2.90}$, WO_3/electrolyte/reference	$\tfrac{1}{0.10} WO_{2.90} + \tfrac{1}{2} O_2 \rightleftharpoons \tfrac{1}{0.10} WO_3$	IV

*The standard states for each reaction are the solid reactant and product in mutual equilibrium at the given temperature.

Suboxides, with oxygen contents corresponding to either extreme of the stoichiometry, were produced by either oxidizing the metal or lower oxide or reducing a higher oxide with an excess of the next higher oxide as an oxidizing agent. The reactions were carried out at 750°C for a minimum of 2 days in a sealed quartz chamber. The X-ray analysis and color of the oxides produced by this method compared well with the data published by Magneli.[15] The electrodes were prepared from the required oxides as described earlier.[12] They contained approximately 80 vol pct of the lower oxygen activity oxide. For each reaction the electromotive-force was measured for a minimum of three cells with both increasing the decreasing temperature. The electromotive-force was taken to be the equilibrium value when three readings at 30-min intervals varied by less than 0.5 mv. Values on heating and cooling and between duplicate cells were in good agreement. Holding times of up to 2 weeks were used when examining the lower-temperature regions. The cells studied did not seriously polarize except at the lowest temperatures. They recovered from momentary polarization currents of several milliamps in less than a day at 850°C. Little reaction of the tungsten rich electrodes with the electrolyte was observed. The higher oxides, especially WO_3, were found to discolor the electrolyte after considerable exposure. Since no drift in electromotive-force for periods up to a month was observed for the $W-WO_2$ and $WO_2-WO_{2.72}$ cells, it was concluded that electrode-electrolyte reactions were not important in these cells. In all cases, the cells used to calculate $\Delta G°$ were stable for periods in excess of 2 weeks.

II) RESULTS AND DISCUSSION

$W-WO_2$. The standard free-energy changes $(\Delta G_1°)$ for the oxidation of tungsten metal to WO_2 were determined from twenty-three cells of type I. Although an unusually large number of cells were used for this determination, only a few points were obtained from many of them. These were used primarily for studying the effects of reference electrode, oxide purity, and metal-oxide ratio, and in attempts to detect the formation of W_3O. Cells using Cu-Cu$_2$O, Fe-Fe$_x$O, and air reference electrodes yielded values of $\Delta G_1°$ that were in excellent agreement, indicating that gas transport between $W-WO_2$ and these reference electrodes was not significant. The $\Delta G_1°$ calculated from all the data are shown in Fig. 1 and can be represented by the least-squares equation $\Delta G_1° = -68,660 + 20.31\,T(°K) \pm 300$ cal per g-atom of oxygen. Early experiments were made with oxides prepared from the dehydrated H_2WO_4. Later experiments were made with the WO_3 produced from oxidized metal. Semi-quantitative analysis of the electrodes after use showed differences of 50 to 200 ppm Si and Fe. The $\Delta G_1°$ for the lower-purity oxides were more negative by 200

cal at 1300°K and 500 cal at 1000°K than those of the higher-purity oxides

As can be seen in Fig. 1 the agreement is good between the $\Delta G_1°$ obtained in this investigation and previous measurements. Most of the previously reported data fall within the ±300 cal uncertainty limits suggested for the equation presented here. The slopes of all the determinations except that of Barbi are very similar.

As can be seen in Fig. 1 Bousquet and Perachon[3] observed a peritectoid reaction at 873°C which they interpreted as the formation of W_3O. They obtained distinct experimental values for the $W-W_3O$ and W_3O-WO_2 equilibria. The data for these two equilibria can be combined, as required, to yield the correct values for the extrapolation of the $W-WO_2$ equilibrium. The electromotive force measurements obtained here do not indicate this peritectoid reaction. No deviations greater than 25 cal were obtained from the linear relation of $\Delta G_1°$ with temperature above 750°C for periods in excess of 3 weeks.

Phillips and Chang[11] were also not able to observe W_3O by X-ray diffraction after prolonged reaction between tungsten-water vapor and tungsten-tungsten trioxide. Thus, the presence of W_3O above 750°C is not supported. Hägg and Schönberg[17] prepared what earlier investigators called β tungsten by the electrolysis of molten salt. The oxide, W_3O, was proposed based on an analysis of their X-ray data. They observed X-ray diffraction lines of α tungsten and WO_2 after heating this material to 750°C for 3 hr. Consequently, measurements were made in the temperature range 600° to 750°C in order to investigate the possibility that W_3O is formed at lower temperatures than were reported by Bousquet and Perachon. Measure-
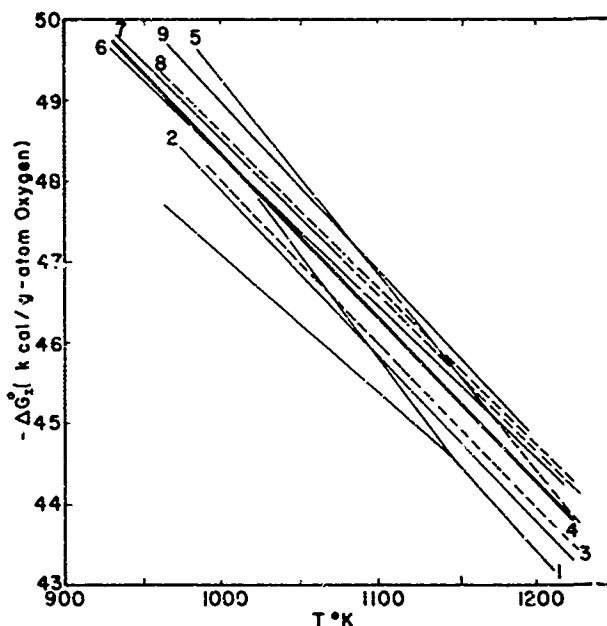

Fig. 1—$\Delta G_1°$ for the reaction $\frac{1}{2}W + \frac{1}{2}O_2 \rightleftharpoons \frac{1}{2}WO_2$: 1, Bousquet and Perachon (gas equilibration);[4] 2, Coughlin (misc);[16] 3, St Pierre et al. (gas equilibration;[1] 4, this investigation (electromotive-force), 5, Barbi (electromotive-force),[2] 6, Vasil'eva et al. (electromotive-force);[6,9] 7 Griffis (gas equilibration);[10] 8, Ackermann and Rauh (effusion);[5] 9, Vasil'eva et al (gas equilibration).[8]

ments in this temperature range are more difficult because of retarded diffusion and reaction rates. Occasionally, deviations from linearity were observed. However, these occurred only with electrodes made from the lower-purity oxides and only when the electrodes were exceedingly tungsten-rich. The deviations from linearity were not reproducible and were of a much larger magnitude than Bousquet and Perachon's data indicated. While the negative results obtained in the 600° to 750°C temperature range are not sufficient to deny the occurrence of W_3O, the weight of evidence is against it. It is probable that the observations of W_3O are due to: 1) impurity effects as suggested by Worrell;[18] 2) a metastable allotrope of tungsten stabilized by small amounts of oxygen as later proposed by Worrell;[19] or 3) a phase stable only under certain experimental conditions of pressure and temperature as has been recently observed in a similar tantalum suboxide.[20]

WO_2-$WO_{2.72}$. The ΔG_{II}° for the oxidation of WO_2 to $WO_{2.72}$ were calculated from six cells of type II using Cu-Cu_2O and air reference electrodes. These data were in good agreement and quite stable with time. Measurements were also made on cells using Fe-Fe_xO and Ni-NiO reference electrodes, but were discarded as they were neither consistent nor stable. Both the direction of the electromotive-force drift and the appearance of the electrodes suggested the occurrence of oxygen transport. The oxygen transport in Cu-Cu_2O vs WO_2-$WO_{2.72}$ cells could be tolerated, even though they have a larger difference in oxygen activity, presumably because of the differences in relative diffusion rates. All the data using Cu-Cu_2O and air reference electrodes may be represented by the linear least-squares equation $\Delta G_{II}^\circ = -59,640$
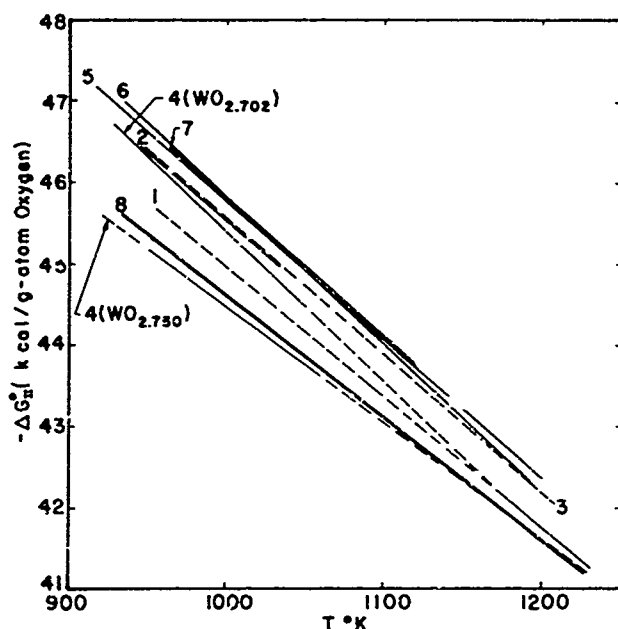

Fig. 2—ΔG_{II}° for the reaction $(1/0.72)WO_2 + \frac{1}{2}O_2$ $\rightleftharpoons (1/0.72)WO_{2.72}$: 1, St. Pierre et al. (gas equilibration);[1] 2, Bousquet and Perachon (gas equilibration);[4] 3, Ackermann and Rauh (effusion);[5] 4, Vasil'eva et al. (electromotive-force);[7] 5, Vasil'eva et al. (electromotive-force);[6] 6, Vasil'eva et al (gas equilibration);[8] 7, Griffis (gas equilibration);[10] 8, this investigation (electromotive-force)

+ 15.01 $T(K) \pm 300$ cal per g-atom of oxygen. The higher-purity oxides yielded values of ΔG_{II}° approximately 200 cal less negative than the lower-purity oxides.

The ΔG_{II}° determined here are presented together with those of other investigators in Fig. 2. Unlike the situation for the W-WO_2 equilibrium our data are considerably less negative than much of the earlier work.[4-10] However, the agreement with St. Pierre et al.[1] and with Vasil'eva et al. (for the single composition $WO_{2.750}$)[9] is quite good. A comparison with the majority of their results is rather difficult. In early work they reported no variation of ΔG_{II}° within the composition limits $WO_{2.39}$-$WO_{2.719}$.[6] These results were in good agreement with their gas equilibration measurements.[8] In a paper covering the compositions $WO_{2.702}$-$WO_{2.750}$, which overlaps the above composition range, they reported less negative results that varied with composition. The range of electromotive-forces covered by this later paper include the values of our observations. Since the electromotive-force is constant throughout a two-phase region, a single-phase region was indicated. If gas transport of oxygen occurred in their experiments, as we suspect, the resulting error would cause the more negative results they reported. The agreement between their results for the composition $W_{2.75}$ and our measurements support this hypothesis. According to Gulbransen[21] the composition limits for $WO_{2.72}$ at 1200°C are $WO_{2.700}$ to $WO_{2.735}$. Thus, $WO_{2.75}$ would appear to be in the $WO_{2.72}$-$WO_{2.90}$ phase field. A reduction of the $WO_{2.750}$ by gaseous transport of oxygen would result in ΔG_{II}° consistent with our measurements in the WO_2-$WO_{2.72}$ phase field.

We favor the less negative results obtained here because of the agreement of ΔG_{II}° obtained with various reference electrodes and the stability and reproducibility of the data.

$WO_{2.72}$-$WO_{2.90}$. The ΔG_{III}° for oxidation of $WO_{2.72}$ to $WO_{2.90}$ were calculated from four cells of type III. Only air reference electrodes were used for these measurements because of the difficulties encountered with gas transport. Our results may be represented by the linear least-squares equation $\Delta G_{III}^\circ = -67,860$ + 24.21 $T(K) \pm 300$ cal per g-atom of oxygen. The experimental scatter for a given cell was somewhat greater than for the first two reactions. This can be attributed to: 1) the smaller amount of oxygen required for this reaction which lowers the buffering capacity of the electrode, increasing sensitivity to leaks; 2) the volatility of $WO_{2.90}$, which was observed to coat the cool ends of the apparatus; and 3) the contamination of the electrolyte. The latter was evident from a surface discoloration that could be observed after prolonged use. Despite the greater experimental scatter for an individual cell, the total scatter for all the cells was similar to that observed for the lower oxides. This would infer that ΔG_{III}° is less sensitive to small changes in purity than either ΔG_I° or ΔG_{II}°.

The ΔG_{III}° determined here are compared with the results of other investigators in Fig. 3. The results of this investigation are in good agreement with the gas equilibration data of Bousquet and Perachon.[4] Two compositions studied by Vasil'eva et al.[7] ($WO_{2.750}$ and $WO_{2.877}$) should fall within the $WO_{2.72}$-$WO_{2.90}$ two-phase

field. As pointed out above, the ΔG°_{III} of $WO_{2.750}$ are more characteristic of WO_2-$WO_{2.72}$ equilibrium. The agreement with their $WO_{2.877}$ data is reasonable considering that their equation represents only four data points obtained from a single cell. The agreement of the results obtained here are only in fair agreement with the work of St. Pierre et al.[1] This is somewhat surprising in view of the excellent agreement for the other reactions studied.

$WO_{2.90}$-WO_3. The ΔG°_{IV} for the oxidation of $WO_{2.90}$ to WO_3 were calculated from only two cells of type IV. However, a total of forty-one measurements were made. Air reference electrodes were used for both of these cells. The results may be represented by the least-squares equation $\Delta G^\circ_{IV} = -66,765 + 26.76\,T(^\circ K)$ ± 500 cal per g-atom of oxygen. These data and the results of other investigators are presented in Fig. 4.*

*Note that the scale in Fig. 4 has been compressed relative to that of the first three figures.

The difficulties involved in studying these oxides is evidenced by the very large range of values of other investigators. Nevertheless, the results presented here are in excellent agreement with the gas equilibrium measurements of both St. Pierre et al.[1] and Bousquet and Perachon.[4] Vasil'eva et al.[7] studied a variety of compositions ($WO_{2.92c}$-$WO_{2.976}$) that should be within the $WO_{2.90}$-WO_3 two-phase field. Their results were not independent of composition but varied by as much as 11 kcal. It should be pointed out that the equations for their data indicate that, for a given temperature, the P_{O_2} in equilibrium with $WO_{2.950}$ is lower than that in equilibrium with $WO_{2.945}$. This casts further doubt on the reliability of the compositions reported in their paper.
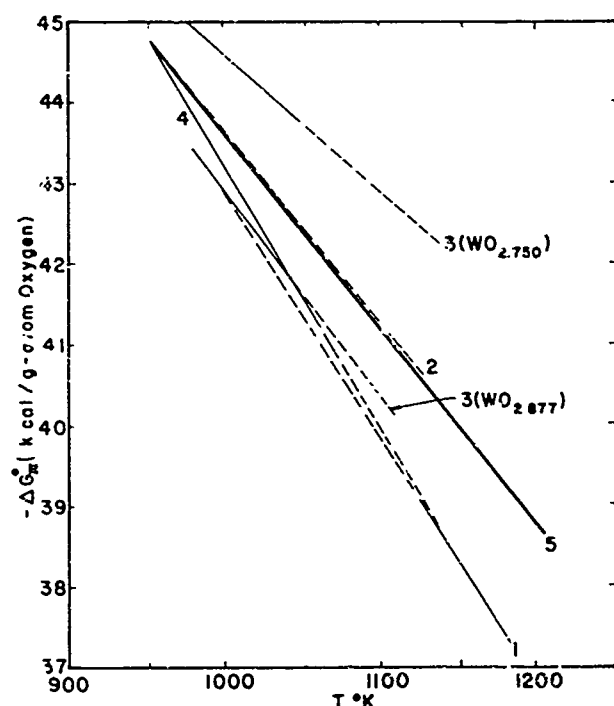

Fig 4—ΔG°_{IV} for the reaction $(1/0.10)WO_{2.90} + \frac{1}{2}O_2$ = $(1/0.10)WO_3$: 1, St. Pierre et al (gas equilibration);[1] 2, Bousquet and Perachon (gas equilibration);[4] 3, Ackermann and Rauh (effusion);[5] 4, Vasil'eva et al. (electromotive-force);[7] 5, Griffis (gas equilibration),[10] 6, this investigation (electromotive-force).

Fig. 3—ΔG°_{III} for the reaction $(1/0.18)WO_{2.72} + \frac{1}{2}O_2$ = $(1/0.18)WO_{2.90}$: 1, St Pierre et al (gas equilibration);[1] 2, Bousquet and Perachon (gas equilibration);[4] 3, Vasil'eva et al. (electromotive-force);[7] 4, Griffis (gas equilibration);[10] 5, this investigation (electromotive-force).
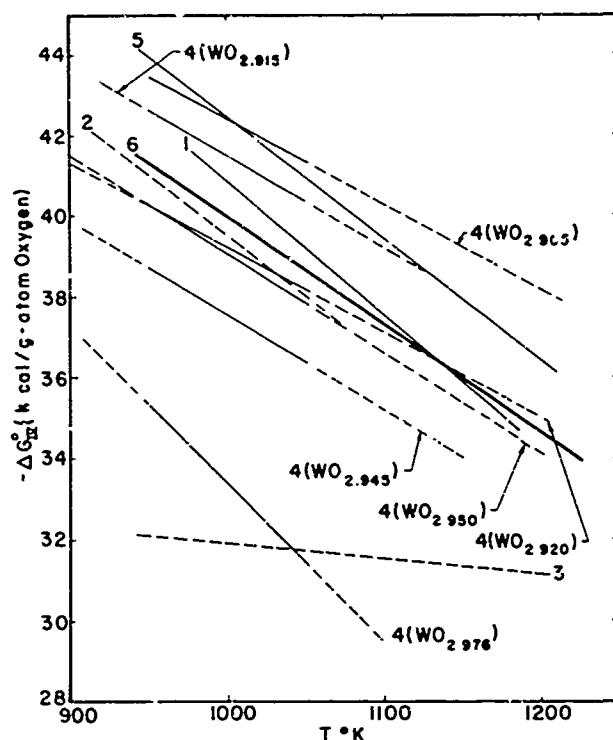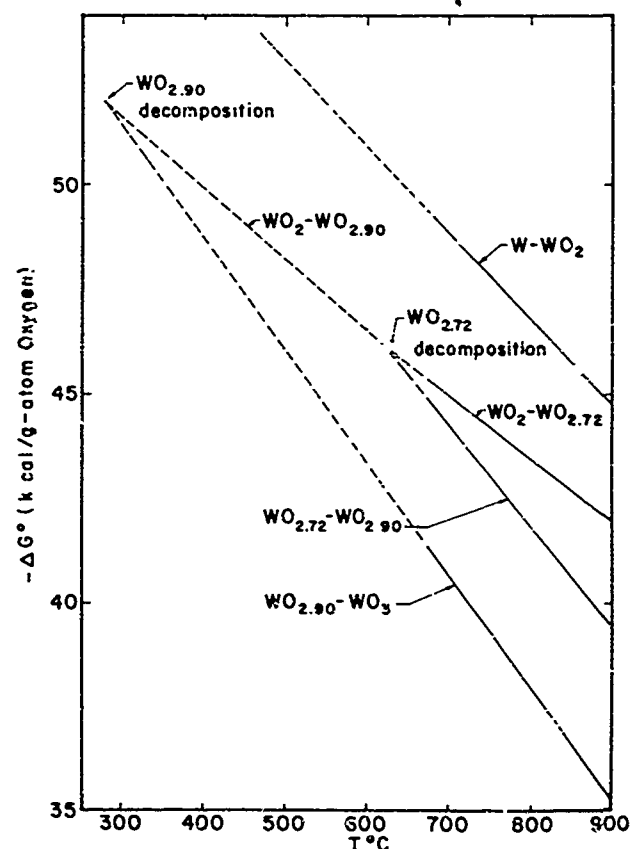

Fig. 5—Summary of ΔG°'s in the W-O system.

Table III

Reaction	ΔG_f°, cal per g-atom of Oxygen	
$\frac{1}{2} W + \frac{1}{2} O_2 \rightleftharpoons \frac{1}{2} WO_2$	$-68,660 + 20.31\ T(^{\circ}K)$	1
$\frac{1}{2.72} W + \frac{1}{2} O_2 \rightleftharpoons \frac{1}{2.72} WO_{2.72}$	$-66,272 + 18.90\ T(^{\circ}K)$	2
$\frac{1}{2.90} W + \frac{1}{2} O_2 \rightleftharpoons \frac{1}{2.90} WO_{2.90}$	$-66,371 + 19.23\ T(^{\circ}K)$	3
$\frac{1}{3} W + \frac{1}{2} O_2 \rightleftharpoons \frac{1}{3} WO_3$	$-56,384 + 19.48\ T(^{\circ}K)$	4

III) GENERAL DISCUSSION

The narrow uncertainty limits indicated above point out the accuracy possible with the solid electrolyte galvanic cell technique. Although the results are not as precise as some obtained for the simpler metal-metal oxide measurements (e.g., Ref. 14), they are more precise than those obtainable by other methods. In general, the agreement with previous gas equilibration measurements, especially those of St. Pierre et al.,[1] is excellent. The generally poor agreement with Vasil'eva et al.[6,7,9] can be attributed to gas transport in their apparatus. They used a disc-type electrolyte which, as mentioned above, permits gas transport. In addition, their data were obtained in vacuum rather than the purified flowing helium atmosphere used in this work. Our experience using an evacuated chamber for this type of apparatus, as well as the experience of others,[22] has been unsatisfactory.

The standard free energies of formation of the four oxides studied can be calculated from the ΔG° presented herein. The values calculated can be represented as shown in Table III. For these calculations the activity of the oxide at either stoichiometry limit is assumed to be the same. This assumption is valid for compounds with small deviations from stoichiometry. The composition limits obtainable from the electromotive-force measurements of Vasil'eva et al.[7] are subject to doubt because of the disagreements pointed out, especially with the higher oxides, and because of the strong probability of uncontrolled gaseous transport of oxygen between the mixed tungsten oxide and reference electrodes. Elsewhere, deviations from stoichiometry of the order of 1 at. pct have been reported.[21] It appears that the assumption of constant activity is reasonable.

As expected, the reported polymorphic transitions in the oxides were not observed. The small change in slope of the free energy of reaction with temperature was undoubtedly masked by the experimental scatter of the technique. The temperatures for the three-phase equilibria WO_2-$WO_{2.72}$-$WO_{2.90}$ and WO_2-$WO_{2.90}$-WO_3 determined from the intersection of the appropriate ΔG°'s are 620° and 280°C, respectively, see Fig. 5. Previous estimates ranged from 506° to 620°C for the WO_2-$WO_{2.72}$-$WO_{2.90}$ equilibrium and 416° to 580°C for the WO_2-$WO_{2.90}$-WO_3 equilibrium.[1,4,11] However, it should be pointed out that a smaller extrapolation was required herein.

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DOCUMENT CONTROL DATA - R & D

(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

1. ORIGINATING ACTIVITY (Corporate author)	2a. REPORT SECURITY CLASSIFICATION
Aerospace Research Laboratories	UNCLASSIFIED
Metallurgy & Ceramics Research Laboratory	2b. GROUP
Wright-Patterson AFB, Ohio 45433	

3. REPORT TITLE

Thermodynamics of the Tungsten-Oxygen System

4. DESCRIPTIVE NOTES *(Type of report and inclusive dates)*

Scientific.   Interim.

5. AUTHOR(S) *(first name, middle initial, last name)*

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Larry R. Bidwell
Darrell F. Frank

6. REPORT DATE	7a. TOTAL NO. OF PAGES	7b. NO. OF REFS
March 1968	5	22

8a. ~~CONTRACT OR GRANT NO.~~ In-House Research	9a. ORIGINATOR'S REPORT NUMBER(S)
b. PROJECT NO. 7021-0005	
c. DoD Element 6144501F	9b. OTHER REPORT NO(S) (Any other numbers that may be assigned this report)
d. DoD Subelement 681306	ARL 68-0057

10. DISTRIBUTION STATEMENT

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11. SUPPLEMENTARY NOTES	12. SPONSORING MILITARY ACTIVITY
Reprint from: TRANSACTIONS OF THE METALLURGICAL SOCIETY OF AIME, Vol. 239, p. 1901-1905, December 1967.	Aerospace Research Laboratories (ARZ) Wright-Patterson AFB, Ohio 45433

13. ABSTRACT

The solid electrolyte galvanic cell technique used to measure the ΔG^o of various reactions of the W-O system in the temperature range 700° to 1000^oC.

DD FORM 1473
1 NOV 65

14. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
electrolyte galvanic cell						
W-O System						